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Implementation of models and data for graphite/water interaction in Spectra

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Summary

This document contains preparatory work for a future analysis of consequences of a water ingress into an HTR reactor with the SPECTRA code. In particular including: - Review of reactions that may take place during water ingress - Selection of models applicable for these reactions - Making necessary extensions to the Material Oxidation Package in SPECTRA, to make sure that it will be possible to model all these reactions. - Comparison of models with available data. Based on this comparison, an extension to the existing correlation of Kubaschewski and Heinrich was proposed, including best estimate as well as conservative multipliers, that depend on the graphite burn-off and total pressure. As a next step, the SPECTRA model of an HTR reference plant (HTR-PM design) will be built and a water ingress scenario will be analyzed.

Approval

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This document contains preparatory work for a future analysis of consequences of a water ingress into an HTR reactor with the SPECTRA code. In particular including:

- Review of reactions that may take place during water ingress
- Selection of models applicable for these reactions
- Making necessary extensions to the Material Oxidation Package in SPECTRA, to make sure that it will be possible to model all these reactions.
- Comparison of models with available data. Based on this comparison, an extension to the existing correlation of Kubaschewski and Heinrich was proposed, including best estimate as well as conservative multipliers, that depend on the graphite burn-off and total pressure.

As a next step, the SPECTRA model of an HTR reference plant (HTR-PM design) will be built and a water ingress scenario will be analyzed.

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1 Introduction

The work described in this report, has been performed within the ARCHER project, Work Package WP22 - Water Ingress.

Direct steam generation coupled to the primary HTR system circuit, necessitates water/steam ingress accident evaluation as a part of safety and licensing analysis. Experience in this field dates back to 1980's, before intermediate heat exchanger and direct primary system turbine cycles were introduced. Currently there is strong evidence that the short to medium term market requires in majority steam supply which re-opens the potential application of direct steam generation.

The work package objective is to assess the potential issues that arise in this type of accidents, and establish a basis for safety evaluation and licensing according to current day standards. This requires the capability of assessing water/steam ingress experimentally, and offers the opportunity with current day advanced computer tools to assess this type of accidents more accurately, and following currently accepted safety standards. Specific attention must be given to temperature dependency of chemical reactions in the reactor core and the potential for formation of flammable or explosive gas mixtures in blow down devices or the reactor building. The experience from the past is available, and will be studied and summarized, as basis and guidance for the efforts in this work package.

One of the tasks to be performed within the ARCHER WP22, is an analysis of consequences of a 2F break (guillotine break with total break area equal two times the tube area) of a single steam generator tube with a two-phase system code SPECTRA. The advantage of using a two-phase system code here is the possibility of modeling the entire system (reactor vessel, steam generator, sub-systems) to calculate the transport of water and steam throughout the reactor system.

This water ingress analysis will be performed in the future. The purpose of the present work is:

- to review reactions that may take place during water ingress,
- to select correlation applicable for these reactions, and
- to implement, if necessary, extensions to the SPECTRA code, in particular to the Material Oxidation Package, to make sure that it will be possible to model all these reactions.

2 SPECTRA Code

2.1 Description of the SPECTRA Code

The SPECTRA code [1] is a computer code developed at NRG, the Netherlands. SPECTRA (Sophisticated Plant Evaluation Code for Thermal-hydraulic Response Assessment) is a fully integrated system code designed for thermal-hydraulic analyses of nuclear or conventional power plants. It is applicable to Light Water Reactors, High Temperature Gas Cooled Reactors, Liquid Metal Reactors.

The program structure is shown in Figure 2-1. The modeling approach is based on the Control Volume (CV) concept. A model of a certain physical system consists of Control Volumes connected by junctions (JN). Within a Control Volume, four fluid components may exist: two continuous components (atmosphere and pool), and two dispersed components (droplets and bubbles). The gas components (atmosphere and bubbles) are assumed to be mixtures of non-condensable gases and steam. Non-equilibrium is assumed between each of the four fluid components, with the inter-component heat and mass transfer modeled in a mechanistic way.

Fluid property tables consist of the properties of water, steam, and several non-condensable gases, are treated as real gases. The water properties are available for temperature range from 273.16 K to critical temperature (647 K). The steam properties were obtained using the NRC/NBC steam tables program interpolated using pre-computed tables, covering the range from 270 K to 3070 K, and from virtually 0.0 Pa to 2.1×10^{7} Pa. Alternatively the user can define fluid properties in input. This way the liquid metal reactor coolants such as sodium or lead, can be used.

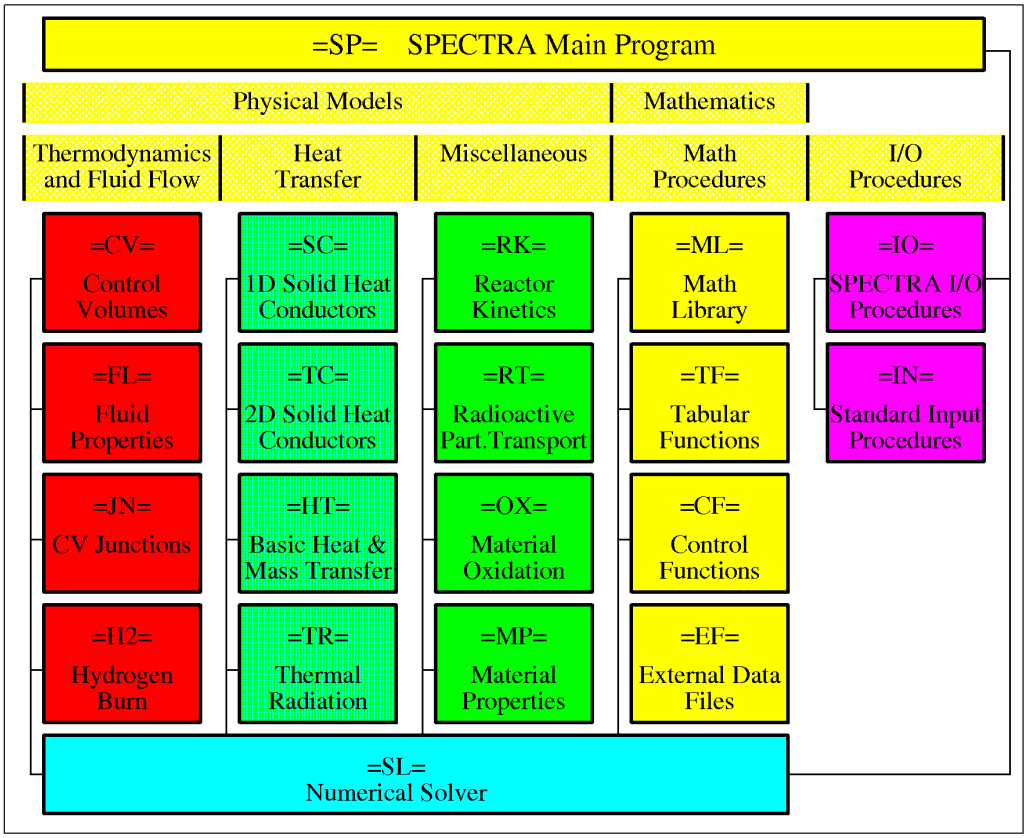

Figure 2-1 : SPECTRA code structure

Heat conduction is calculated by the 1-D and 2-D Solid Heat Conductor Packages, using a general transient heat conduction equation, The heat transfer at the boundaries of the Solid Heat Conductors is obtained from the Heat and Mass Transfer Package, which provides models for natural and forced convection, condensation with and without non-condensable gases, nucleate boiling, critical heat flux, transition boiling, Leidenfrost transition, film boiling, heat transfer in two-phase flow, as well as non-equilibrium boiling and condensation ("flashing" and "fogging"). The heat and mass transfer models include correlations valid for wall-fluid, pool-atmosphere, atmosphere-droplets, and pool-bubbles interfaces. Models for the bubble collapse as well as the heat and mass transfer to bubbles in swarms are included (see reference [1] for details).

A detailed thermal radiation model is provided, including grey enclosure models, with and without participating gas. The gas radiation model is based on the Hottel gas approach, [11].

The point reactor kinetics model is available, with reactivity feedback from control rods, fuel temperature, moderator temperature, void fraction, as well as changes in isotope concentrations. The Isotope Transformation model is available as a part of the Reactor Kinetics Package. It allows computing core composition changes (due to fuel burn-up, production of poisons, such as Xe-135, fuel reload, etc.), and their effect on reactivity as well as decay heat production. The model is based mainly on data from references [12], [13].

The Radioactive Particle Transport Package deals with release of fission products, aerosol transport, deposition, and resuspension. Radioactive chains of fission products are tracked. The models for the transport and deposition of aerosols include Brownian diffusion, thermophoresis, and gravitational settling. For turbulent flow conditions, turbulent deposition models for the diffusional deposition, turbulent eddy impaction, and inertia impaction regime are included. Moreover, gravitational, Brownian, and turbulent coagulation are modeled. Two state-of-the-art dynamic resuspension models are available. Alternatively, resuspension can be modeled using a parametric model with user-defined coefficients directly obtained from resuspension experiments (see reference [1] for details).

A hydrogen burn model is available, which includes slow deflagrations, fast turbulent deflagrations, and detonations. The model is based mainly on data from reference [14].

An oxidation model is available that contains models for zircaloy, steel oxidation by steam and oxygen, carbon oxidation by oxygen, as well as a general oxidation equation with user-defined coefficients. Via this equation any oxidation reaction may be modeled. Multiple reactions (for example simultaneous oxidation of zircaloy by steam and oxygen) are possible (see reference [1] for details).

On top of the models mentioned above, general-purpose utilities, called Tabular Functions, Control Functions, are available. With these functions the user can define certain quantities in the physics packages. They can be applied for example:

- to provide boundary conditions to the analyzed problem,
- to model control systems of a reactor,
- to model safety system activations; etc.

The Numerical Solver Package is responsible for solving all Packages simultaneously, using a stable implicit solution scheme. Control Functions are included in the implicit solution, which allows solving stiff differential equations. The solution scheme allows performing calculations without making practically any mass or energy error. The SPECTRA program performs a global mass and energy check at the end of each time step. In absence of the thermal radiation model, the mass and energy errors are caused only by round-off errors of double precision arithmetics, which give relative errors of order of 10^{-15}.

The SPECTRA code provides extensive diagnostics of input data. All input entries are checked for consistency. Errors and warning messages are given in a separate file. These messages allow an easy correction of input errors and inconsistencies.

2.2 Description of the Material Oxidation Package in SPECTRA

This section gives a short description of the Material Oxidation Package (=OX=) in SPECTRA. The description provided in this section is taken from the SPECTRA Version 3.60 Code Manual, Volume 1 - Program Description.

2.2.1 Introduction

In SPECTRA a general material oxidation model is available for all 1-D and 2-D solid structure surfaces. For every surface (left and right surface for 1-D structures, boundary cell surface for 2-D structures) the user may specify one or more oxidation reactions. If more than one reaction is specified (for example oxidation by steam and oxygen), both reaction will proceed in parallel, according to their own reaction kinetics and availability of the oxidizing media (steam, oxygen). Several reactions are built-in and may be simply selected from the list. The built-in reactions are described in section 2.2.2. Other reactions may be built by specifying coefficients determining reaction kinetics, reaction heat, etc. The user-defined reactions are described in section 2.2.3.

2.2.2 Built-In Oxidation Reactions

The following built-in reactions are available:

- Oxidation by steam
  - Zircaloy + H_2O, model of Cathcart and Urbanic-Heidrich
  - Zircaloy + H_2O, model of Urbanic-Heidrich
  - Steel + H_2O, model of White
- Oxidation by O_2
  - Zircaloy + O_2, model of Benjamin et al.
  - Graphite + O_2 model of Roes

These reactions and modeling are described in detail in the SPECTRA Code Manuals [1] and are not further discussed here. The graphite-steam reaction is modeled using a user-defined reaction, discussed in the next section.

2.2.3 User-Defined Oxidation Reactions

In SPECTRA Version 3.60 [1], any reaction may be modeled through a user-defined oxidation model. All coefficients for such reactions must be defined by the user. The oxidation reaction is assumed to have the form:

$$Mt + n_1\ Gs_1 \rightarrow MtOx + n_2\ Gs_2$$

Mt	material to be oxidized
MtOx	material oxide
Gs_1	gas 1 (oxidizing gas, for example steam, oxygen
Gs_2	gas 2 (product of reaction, for example hydrogen)
n_1	reaction ratio 1 - moles of gas Gs_1 per one mole of material to be oxidized
n_2	reaction ratio 2 - moles of gas Gs_2 per one mole of material to be oxidized

The reaction kinetics is assumed to be given by the following general formula:

$$\frac{dm^x}{dt} = K(T, v, p_i)$$

m	mass of material to be oxidized per unit surface area [kg/m^2]
x	exponent, [-] (user-defined, *x*=2 for a parabolic oxidation rate)

t	time [s]
K	reaction rate [(kg/m^2)x/s]
T	temperature, [K]
v	velocity of the oxidizing gas, [m/s]
p_i	partial pressure of the gas i, [Pa]

When the reaction rate term, K, is written explicitly, the formula determining the reaction kinetics becomes:

$$\frac{dm^x}{dt} = \left(\frac{1}{K_T(T)} + \frac{1}{K_v(v,T)} \right)^{-1} \cdot K_p(p_1)$$

The terms, $K_T(T)$, $K_v(v,T)$, $K_p(p)$, are described below.

- Temperature-dependent coefficient, $K_T(T)$:

$$K_T(T) = \begin{cases} A_1 \exp\left[-B_1/T\right] & for\ T < T_1 \\ A_2 \exp\left[-B_2/T\right] & for\ T > T_2 \end{cases}$$

A_1	coefficient for reaction rate at low temperatures, [(kg/m^2)^x/s]
B_1	coefficient for reaction rate at low temperatures, [K]
T_1	upper temperature limit to apply the low temperature kinetics equation, [K]
A_2	coefficient for reaction rate at high temperatures, [(kg/m^2)^x/s]
B_2	coefficient for reaction rate at high temperatures, [K]
T_2	lower temperature limit to apply the high temperature kinetics equation, [K]

The above coefficients are defined by the user in the input deck. Additionally minimum and maximum temperature limits, T_{min}, T_{max}, are defined. The oxidation rate is set to zero for $T<T_{min}$. A linear interpolation from zero to a full value is performed between T_{min} and T_{min}+ 10.0 K. If $T>T_{min}$ then T_{min} is used to evaluate $K_T(T)$, as well as $K_v(v,T)$.

- Velocity-dependent coefficient, $K_v(v,T)$:

$$K_v(v,T) = C \cdot v^D \cdot T^E$$

v	gas velocity, [m/s]
T	temperature, [K]
C	user-defined coefficient determining the reaction rate, [kg^x m^{-2x-D} s^{-1+D} K^{-E}]
D	user-defined exponent, [-]
E	user-defined exponent, [-]

Minimum and maximum velocity limits, v_{min}, v_{max}, are applied. If $v<v_{min}$ then v_{min} is used to evaluate $K_v(v,T)$. If $v>v_{max}$ then the v_{max} is used to evaluate $K_v(v,T)$.

- Pressure-dependent coefficient, $K_p(p_1)$:

$$K_p(p) = \left(\frac{p}{p_{ref}} \right)^F$$

p_1	partial pressure of the oxidizing gas (Gs_1), [Pa]
p_{ref}	user-defined reference pressure, [Pa]
F	user-defined exponent, [-]

Minimum and maximum pressure limits, p_{min}, p_{max}, are applied. The oxidation rate is set to zero for $p_1<p_{min}$. A linear interpolation from zero to a full value is performed between p_{min} and p_{min}×2.0. If $p_1>p_{max}$ then p_{max} is used to evaluate $K_p(p_1)$.

3 Implementation of Models for Primary C-H_2O Reaction

3.1 Modifications in the SPECTRA Code

Within the current task, several extensions were made to the user-defined oxidation model, to allow modeling graphite-steam reaction modeling. The code version with implemented changes is 3.61. The description below is taken from the SPECTRA Version 3.61 Code Manual, Volume 1 - Program Description.

In the new SPECTRA Version 3.61, the oxidation reaction is assumed to have the form:

$$Mt + n_1\ Gs_1 \rightarrow MtOx + n_2\ Gs_2 + n_3\ Gs_3$$

Mt material to be oxidized
MtOx material oxide
Gs_1 gas 1 (oxidizing gas, for example steam, oxygen
Gs_2 gas 2 (product of reaction, for example hydrogen)
Gs_3 gas 3 (optional second product of reaction)
n_1 reaction ratio 1 - moles of gas Gs_1 per one mole of material to be oxidized
n_2 reaction ratio 2 - moles of gas Gs_2 per one mole of material to be oxidized
n_3 reaction ratio 3 - moles of gas Gs_3 per one mole of material to be oxidized

Compared to the previous code version (see section 2.2.3), the second reaction product gas has been added, Gs_3, n_3. This was necessary because there are two gaseous products of the reaction.

The general formula for reaction kinetics has also been extended, as follows:

$$\frac{dm^x}{dt} = K(T, v, p_i) \cdot M(B,...)$$

m mass of material to be oxidized per unit surface area [kg/m^2]
x exponent, [-] (user-defined, *x*=2 for a parabolic oxidation rate)
t time [s]
K reaction rate [(kg/m^2)^x/s]
T temperature, [K]
v velocity of the oxidizing gas, [m/s]
p_i partial pressure of the gas *i*, [Pa]
M(*B*,...) multiplier to account for the effect of burn-off and eventual other parameters

When the reaction rate term, *K*, is written explicitly, the formula determining the reaction kinetics becomes:

$$\frac{dm^x}{dt} = \left(\frac{1}{K_T(T) \cdot C_T(T, p_i)} + \frac{1}{K_v(v,T)} \right)^{-1} \cdot K_p(p_1) \cdot M(B,...)$$

Compared to the previous code version, the terms $C_T(T, p_i)$, $M(B,...)$, have been added. The terms, $K_T(T)$, $K_v(v,T)$, $K_p(p)$, are described in section 2.2.3. The new terms, $C_T(T, p_i)$, $M(B,...)$, are described below.

- Correction to temperature-dependent coefficient, $C_T(T, p_i)$:

$$C_T(T, p_1, p_2, p_3) = \frac{1}{1 + A_3\ \exp[B_3 / T] \cdot p_1^{X_1} \cdot p_2^{X_2} \cdot p_3^{X_3}}$$

C_T correction to the temperature-dependent reaction rate, [-],
A_3 first coefficient, [-],
B_3 second coefficient, [K],

p_1 partial pressure of the gas Gs_1 (oxidizing gas), [Pa],
p_2 partial pressure of the gas Gs_2 (first reaction product), [Pa],
p_3 partial pressure of the gas Gs_3 (second reaction product), [Pa],
X_1 exponent for the gas Gs_1
X_2 exponent for the gas Gs_2
X_3 exponent for the gas Gs_3

- Multiplier to account for the effect of burn-off and eventual other parameters, $M(B, ...)$:

  Most oxidation reactions slow down when material is oxidized and a protective layer of oxide is built. This fact is taken into account in correlations by using exponent x (typically taken as 2 - parabolic reaction rate). For some reactions, for example graphite oxidation: $C+O_2 \rightarrow CO_2$ or $C+H_2O \rightarrow H_2+CO$, there is no oxide build-up. The reaction speeds up in time because of an increased surface area due to micro cavities created when graphite is burned off. This fact can be taken into account by using the burn-off function $M(B,...)$. No correlation is provided here, $M(B,...)$ must be defined by the user, via a Tabular Function, TF(d_{ox}) or a Control Function, CF. If TF is used, the argument is always the depth of oxidized material, d_{ox}. If a Control Function is used, then this factor may be a function of any parameter.

3.2 Correlation

The primary heterogeneous reaction is graphite oxidation by steam. The reaction is:

$$C + H_2O \rightarrow H_2 + CO$$

Reference [8] recommends the correlation from Kubaschewski and Heinrich [2], to calculate the reaction kinetics. The correlation is:

$$\frac{dm}{dt} = \frac{6.4 \cdot 10^{11} \cdot \exp\left[-\frac{256{,}000}{8.315 \cdot T}\right] \cdot p_{H2O}^{0.44}}{1 + 7.5 \cdot 10^{-5} \cdot \exp\left[\frac{121{,}000}{8.315 \cdot T}\right] \cdot p_{H2}^{0.9} \cdot p_{H2O}^{-0.4}}$$

Here pressure is in [bar], and reaction rate in [mg/cm^2-hr]. First, the formula is converted to SI units:

$$\frac{dm}{dt} = \frac{1.78 \cdot 10^{6} \cdot \exp\left[-\frac{256{,}000}{8.315 \cdot T}\right] \cdot \left(\frac{p_{H2O}}{10^5}\right)^{0.44}}{1 + 7.5 \cdot 10^{-5} \cdot \exp\left[\frac{121{,}000}{8.315 \cdot T}\right] \cdot \left(\frac{p_{H2}}{10^5}\right)^{0.9} \cdot \left(\frac{p_{H2O}}{10^5}\right)^{-0.4}}$$

Here pressure is in [Pa], reaction rate in [kg/m^2-s] and temperature in [K]. Furthermore, the formula is rearranged as follows:

$$\frac{dm}{dt} = \frac{1.12 \cdot 10^{4} \cdot \exp\left[-\frac{30788}{T}\right] \cdot \left(p_{H2O}\right)^{0.44}}{1 + 2.37 \cdot 10^{-7} \cdot \exp\left[\frac{14552}{T}\right] \cdot \left(p_{H2}\right)^{0.9} \cdot \left(p_{H2O}\right)^{-0.4}}$$

For the purpose of test calculations in SPECTRA, the reaction rate is defined using the temperature-dependent factor $K_T(T)$, the correction to the temperature-dependent factor $C_T(T,p_i)$, and the pressure-dependent factor, $K_p(p_1)$:

- Temperature-dependent coefficient, $K_T(T)$:

$$K_T = 1.12 \cdot 10^4 \cdot \exp\left[-\frac{30788}{T}\right]$$

- Correction to temperature-dependent coefficient, $C_T(T, p_i)$:

$$C_T = \frac{1}{1 + 2.37 \cdot 10^{-7} \cdot \exp\left[\frac{14552}{T}\right] \cdot (p_{H2})^{0.9} \cdot (p_{H2O})^{-0.4}}$$

- Pressure-dependent coefficient, $K_p(p_1)$:

$$K_p = (p_{H2O})^{0.44}$$

The reaction heat, 131.3 kJ/mol = 131.3×10^6 [J/kmol] = 10.9×10^6 [J/kg] (per unit mass of oxidized C).

3.3 Verification and Validation

The description below is taken from the SPECTRA Version 3.61 Code Manual, Volume 4 - Verification and Validation.

3.3.1 Verification

Three test cases were chosen (arbitrarily) to perform verification:

- Case 1 - H_2O at p_{H2O} = 70.00 bar (pure steam)
- Case 2 - H_2O at p_{H2O} = 66.09 bar, H_2 at p_{H2} = 3.914 bar
- Case 3 - H_2O at p_{H2O} = 22.03 bar, H_2 at p_{H2} = 47.49 bar

Results of SPECTRA calculations are compared below to hand calculation (obtained using a spreadsheet). The SPECTRA values were obtained from the time-dependent graphs, at the time at which the initially 1 mm thick layer of graphite disappears. There is a good agreement between the hand calculation and the SPECTRA-calculated values.

		Case 1	Case 2	Case 3	
	T=	1273.0	1273.0	1273.0	K
	p(H2O)=	70.00	66.09	22.03	bar
	p(H2)=	0.000	3.914	47.970	bar
	f(B)=	1.000	1.000	1.000	-
Correlation:	dm/dt=	130.2	23.4	1.2	mg/cm2-hr
converted to SI:	dm/dt=	3.62E-04	6.51E-05	3.28E-06	kg/m2-s
directly in SI:	dm/dt=	3.61E-04	6.50E-05	3.27E-06	kg/m2-s
	ρ=	2250.0	2250.0	2250.0	kg/m3
	dx/dt=	1.6E-07	2.9E-08	1.5E-09	m/s
	dx/dt=	1.6E-04	2.9E-05	1.5E-06	mm/s
	τ=	6233	3.459E+04	6.873E+05	s/mm
SPECTRA:	τ=	6233	3.459E+04	6.874E+05	s/mm

3.3.2 Validation

Validation is performed by comparing results of correlation with results available experimental data, obtained from references [3], [5] and in one case from an analytical model, reference [4].

- Oxidation at different steam pressures - validation (code-to-experiment) against data of Loenißen [3]

Experiments were performed at 2.9 bar total pressure and 1000˚C. Page 95 of reference [3] gives oxidation results for several steam pressures. The results obtained from the correlation are compared to the experimental data below.

Test Case Loenissen 1

		1000	1000	1000	1000	˚C	
	T=	1273.0	1273.0	1273.0	1273.0	K	
	p(H2O)=	0.066	0.243	0.394	0.973	bar	
	p(H2)=	0.000	0.000	0.000	0.000	bar	
	M(B,P)=	1.00E+00	1.00E+00	1.00E+00	1.00E+00	-	P=2.9 bar
Correlation:	dm/dt=	6.07E+00	1.08E+01	1.33E+01	1.98E+01	mg/cm2-hr	
converted to SI:	dm/dt=	1.69E-05	2.99E-05	3.70E-05	5.51E-05	kg/m2-s	
directly in SI:	dm/dt=	1.69E-05	3.00E-05	3.71E-05	5.52E-05	kg/m2-s	
Data, p. 95:	dm/dt=	1.78E-03	4.17E-03	4.39E-03	9.72E-03	mg/cm2-s	
	dm/dt=	1.78E-05	4.17E-05	4.39E-05	9.72E-05	kg/m2-s	
Ratio:		1.05	1.39	1.18	1.76		

Conclusion:
Values obtained from the investigated correlation
need to be multiplied by a factor of 1.05 - 1.76 to match the considered data

It is concluded that the correlation gives reaction rates lower than the experimental data. In order to best represent the measured data, the values obtained from the correlation should be multiplied by:

$$Data = (1.05 \div 1.76) \times Correlation$$

- Electrode graphite oxidation - validation (code-to-experiment) against data of Abel-Holden [5]

Reference [5] shows data for graphite steam reaction. Page 7 shows reaction rate of 0.0126 g/min measured for a rectangular prism, 7.9×7.9×31.7 mm specimen, placed in steam at 1900˚F. The value converted to SI units is 1.86×10^{-4} kg/m^2-s. The correlation gives for this case 1.12×10^{-4} kg/m^2-s. Results of calculations are shown below.

Test Case Abel-Holden

		1900	1900	1900	˚F			
		2359.67	2359.67	2359.67	˚R	Dimensions:		
	T=	1310.9	1310.9	1310.9	K	A=	1.13E-03	m2
	p(H2O)=	1.00	1.00	1.00	bar	L=	0.0317	m
	p(H2)=	0.000	0.000	0.000	bar	a=	0.0079	m
	M(B,P)=	1.00E+00	1.67E+00	1.80E+00	-	b=	0.0079	m
			(best est.)	(conserv.)		Measured:		
Correlation:	dm/dt=	40.4	67.5	72.8	mg/cm2-hr	dM/dt=	0.0126	g/min
converted to SI:	dm/dt=	1.12E-04	1.87E-04	2.02E-04	kg/m2-s	dM/dt=	2.10E-07	kg/s
directly in SI:	dm/dt=	1.12E-04	1.87E-04	2.02E-04	kg/m2-s	dm/dt=	1.86E-04	kg/m2-s
	ρ=	2250.0	2250.0	2250.0	kg/m3			
	dx/dt=	5.0E-08	8.3E-08	9.0E-08	m/s			
	dx/dt=	5.0E-05	8.3E-05	9.0E-05	mm/s			
	τ=	20075	12021	11153	s/mm			
SPECTRA:	τ=	20090	12030	11160	s/mm			
	Ratio:	1.66	1.00	0.92				

Conclusion:
Values obtained from the investigated correlation
need to be multiplied by a factor of 1.66 to match the considered data

It is concluded that the correlation gives reaction rate lower than the experimental data. In order to best represent the measured data, the values obtained from the correlation should be multiplied by:

$$Data = (1.66) \times Correlation$$

The values of best estimate and conservative multiplier M(B,P), will be explained below. One has to keep in mind that experiments reported in [5] were performed for electrode graphite, not nuclear graphite.

- Oxidation at low steam pressure - validation (code-to-code) against data of Xinli Yu, Suyuan Yu [4]

Reference [4] provides an analytical estimation of the amount of oxidation that can occur at low steam pressures. This may occur in the HTR system if helium is not sufficiently purified. Also humidity of air can be absorbed and stored in the outer part of the graphite spheres, since the pebbles are not always stored under exclusion of air. The value mentioned is 280 kg of graphite oxidized per year at steam partial pressure of 14 Pa. Considering that the number of pebbles is 420,000 and the fuel-free zone of pebbles is 5 mm [4], this corresponds to oxidation of 0.62% of the fuel-free zone, or oxidation depth of 3.1×10^{-5} m. The value obtained from the correlation is 0.73 year. Results of calculations are shown below.

Test Case Xinli Yu, Suyuan Yu

		750	750	750	˚C		HTR=PM
	T=	1023.0	1023.0	1023.0	K	N=	420000
	p(H2O)=	1.40E-04	1.40E-04	1.40E-04	bar	D=	0.06
	p(H2)=	0.000	0.000	0.000	bar	d-free=	0.005
	M(B,P)=	1.00E+00	6.30E-01	1.80E+00	-	rho=	2250
			(best est.)	(conserv.)		V-free=	4.76E-05
	dm/dt=	1.10E-03	6.91E-04	1.97E-03	mg/cm2-hr	V=	2.00E+01
	dm/dt=	3.0E-09	1.9E-09	5.5E-09	kg/m2-s	M=	4.50E+04
	ρ=	2250.0	2250.0	2250.0	kg/m3	V-pebb=	1.13E-04
	dx/dt=	1.4E-12	8.5E-13	2.4E-12	m/s	M-pebb=	2.54E-01
	dx/dt=	1.4E-09	8.5E-10	2.4E-09	mm/s		
	τ=	7.38E+08	1.17E+09	4.10E+08	s/mm		
		205131	325605	113962	hr/mm		
		23.42	37.17	13.01	years		
						Data:	
To oxidize:	d-OX=	3.100E-05	3.100E-05	3.100E-05	m	280	kg per year
of:	d-free=	5.0E-03	5.0E-03	5.0E-03	m	280 kg is:	
	Oxidized=	0.62	0.62	0.62	%	0.62	%
Correlation:	τ=	2.29E+07	3.63E+07	1.27E+07	s	of the fuel-free zone	
		6359.1	10093.7	3532.8	hr	oxidized per	
		0.73	1.15	0.40	years	1.00	year

Conclusion:
Values obtained from the investigated correlation
need to be multiplied by a factor of 0.73 to match the considered data

It is concluded that:

- The correlation can be applied at very low steam pressure.
- The correlation gives reaction rate higher than the reference data. In order to best represent the measured data, the values obtained from the correlation should be multiplied by:

$$Data = (0.73) \times Correlation$$

The values of best estimate and conservative multiplier $M(B,P)$, will be explained below.

- Effect of burn-off

Burn-off increases reaction rate because the surface area accessible for oxidation reaction increases by formation of geometrically regular pits, which seems to be an inherent feature of graphite oxidation [7]. The surface area increases until a certain value, at which the whole surface is covered by pits, upon which there is no further effect of burn-off - see Figure 3-1. A detailed discussion of the subject is provided in [7].

There are two main parameters of interest here:

- Oxidation depth (burn-off), B_{max}, at which the area increase reaches maximum.
- Maximum area increase factor, $f_{max} = f(B_{max})$

Several correlations were proposed to calculate the burn-off factor, $f(B)$. Reference [4] gives:

$$f(B) = (1-B)\cdot(1-\xi_0 \cdot \ln(1-B))^{0.5}$$

Here B is burn-off [-] and ξ_0 is a constant, equal to 45. The results of the correlation is shown in Figure 3-2.

Reference [6] gives another correlation:

$$f(B) = 0.477 + 0.8094\cdot B - 0.3221\cdot B^2 + 0.0681\cdot B^3 - \\ - 0.00613\cdot B^4 + 12.32\cdot 10^{-6}\cdot B^5 + 2.89\cdot 10^{-5}\cdot B^6 - 1.15\cdot 10^{-6}\cdot B^7$$

Here B is in % and is valid from 1 to 13%, beyond which the 13% value should be used. The results of the correlation is shown in Figure 3-3.

Summarizing, both correlations give $f(B)$ increasing from 1.0 (at B = 0.0) to a maximum of f_{max} = 3.0 (at $B = B_{max}$). The discussion above is only to introduce the problem of burn-off and show a qualitative behavior. Neither of these correlations is used, but a fit to available data is developed, which is shown below.

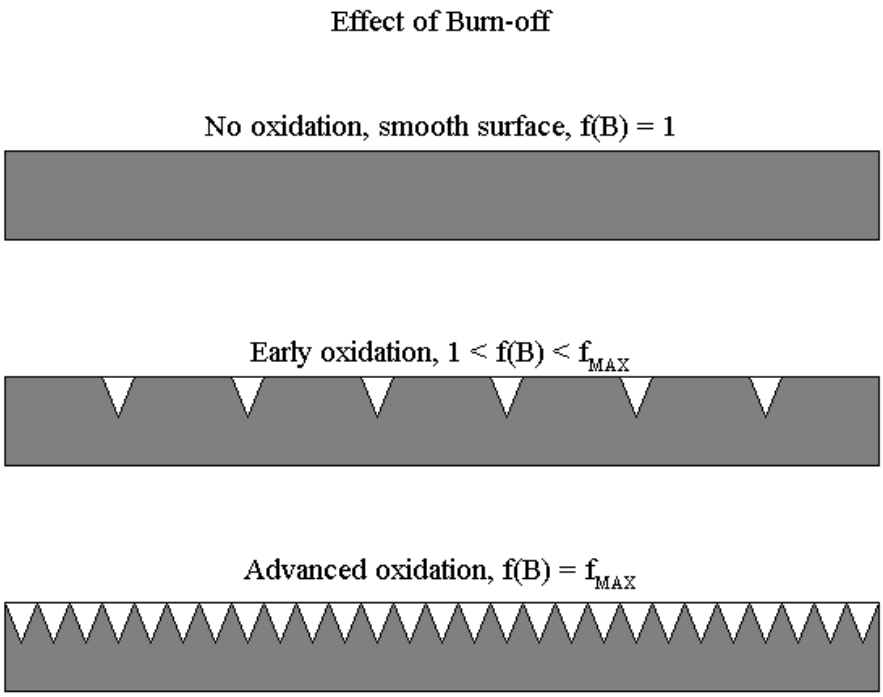

Figure 3-1 : Increase of effective oxidation area due to graphite burn-off

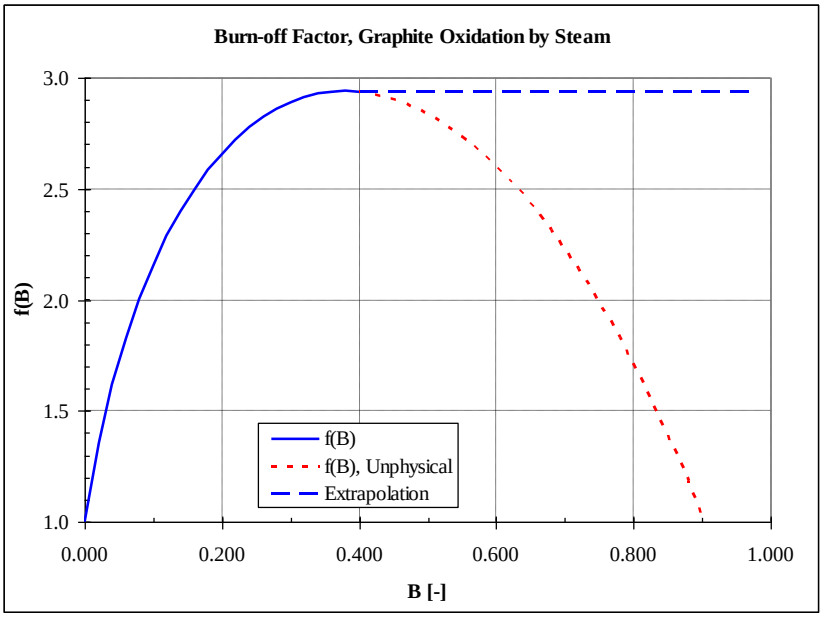

Figure 3-2 : Burn-off correlation from [4]

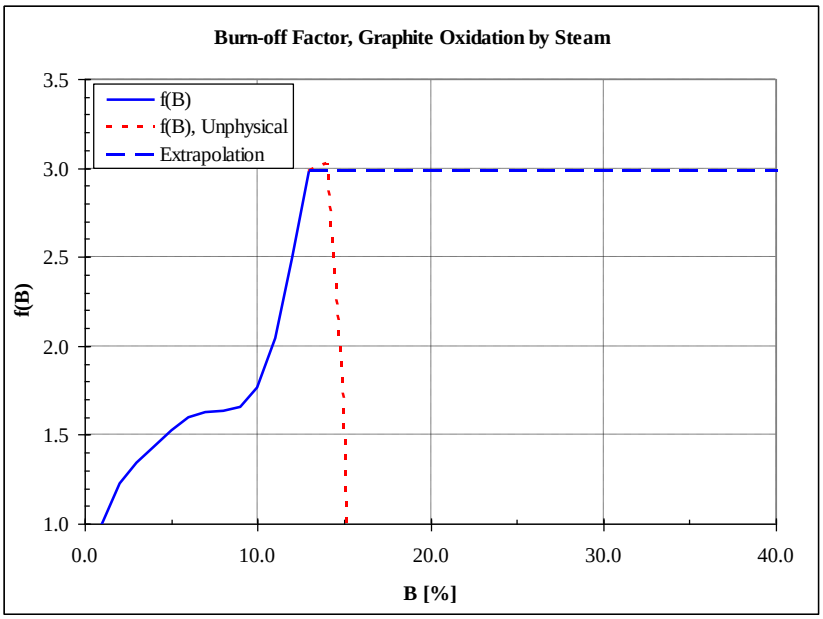

Figure 3-3 : Burn-off correlation from Graphite Design Handbook [6]

- Oxidation at different burn-offs - validation (code-to-experiment) against data of Loenißen [3]

Experiments were performed at 0.474 bar steam pressure and 1000˚C. Reference [3] gives oxidation results for different burn-off values. The results obtained from the correlation are compared to the experimental data below. It should be noted that the burn-off, as well as the total pressure, are not taken into account in the correlation.

Test Case Loenissen 2

	Burn-off:	1	40	60	80	mg/cm2
	Burn-off:	4.44E-06	1.78E-04	2.67E-04	3.56E-04	m
		1000	1000	1000	1000	˚C
	T=	1273.0	1273.0	1273.0	1273.0	K
	p(H2O)=	0.474	0.474	0.474	0.474	bar
	p(H2)=	0.000	0.000	0.000	0.000	bar
	M(B,P)=	1.00E+00	1.00E+00	1.00E+00	1.00E+00	-
Correlation:	dm/dt=	1.45E+01	1.45E+01	1.45E+01	1.45E+01	mg/cm2-hr
converted to SI:	dm/dt=	4.02E-05	4.02E-05	4.02E-05	4.02E-05	kg/m2-s
directly in SI:	dm/dt=	4.01E-05	4.01E-05	4.01E-05	4.01E-05	kg/m2-s
	ρ=	2250.0	2250.0	2250.0	2250.0	kg/m3

Data from Table 5:

	Burn-off:	~1	~40	~60	~80	mg/cm2
at 3 bar:	dm/dt=	1.33E-03	6.13E-03	6.54E-03	6.45E-03	mg/cm2-s
at 4 bar:	dm/dt=	1.49E-03	-	-	-	mg/cm2-s
at 7 bar:	dm/dt=	1.20E-03	5.14E-03	5.54E-03	-	mg/cm2-s
at 15 bar:	dm/dt=	1.11E-03	-	5.16E-03	4.81E-03	mg/cm2-s
at 40 bar:	dm/dt=	-	2.36E-03	2.75E-03	3.12E-03	mg/cm2-s
at 55 bar:	dm/dt=	-	2.14E-03	2.51E-03	-	mg/cm2-s

Converted to SI:

	Burn-off:	~0.0	~2E-4	~3E-4	~4E-4	m
at 3 bar:	dm/dt=	1.33E-05	6.13E-05	6.54E-05	6.45E-05	kg/m2-s
at 4 bar:	dm/dt=	1.49E-05	-	-	-	kg/m2-s
at 7 bar:	dm/dt=	1.20E-05	5.14E-05	5.54E-05	-	kg/m2-s
at 15 bar:	dm/dt=	1.11E-05	-	5.16E-05	4.81E-05	kg/m2-s
at 40 bar:	dm/dt=	-	2.36E-05	2.75E-05	3.12E-05	kg/m2-s
at 55 bar:	dm/dt=	-	2.14E-05	2.51E-05	-	kg/m2-s

Ratio:

	Burn-off:	~0.0	~2E-4	~3E-4	~4E-4	m	
at 3 bar:	corr/exp=	0.33	1.53	1.63	1.61	-	
at 4 bar:	corr/exp=	0.37	-	-	-	-	
at 7 bar:	corr/exp=	0.30	1.28	1.38	-	-	
at 15 bar:	corr/exp=	0.28	-	1.29	1.20	-	
at 40 bar:	corr/exp=	-	0.59	0.69	0.78	-	
at 55 bar:	corr/exp=	-	0.53	0.63	-	-	
				Min=	0.28		-72%
				Max=	1.63		63%

Conclusion:
Values obtained from the investigated correlation need to be multiplied by a factor of 0.28 - 1.63 to match the considered data

It is concluded that in order to best represent the measured data, the values obtained from the correlation should be multiplied by:

$$Data = (0.28 \div 1.63) \times Correlation$$

This is quite a large spread of measured data compared to the results of the correlation. This fact was a motivation to develop an extension to the existing correlation. This extension, as well as the resulting improvement in the obtained accuracy, are described below.

- Extension of the Kubaschewski-Heinrich correlation

Based on the results of Loenißen, the following observations are made:

- At low burn-off, B = 0.0 (clean surface) the correlation should be multiplied by 0.28 - 0.37. The value decreases slightly with total pressure.
- At high burn-offs, B_{max}, the correlation should be multiplied by 1.5 - 1.6 at low pressures and 0.7 - 0.8 at high pressures.
- A surface can be considered as “high burn-off”, B_∞, for 0.3 mm oxidation depth.

Based on the above observations, a multiplier, $M_{BE}(B,P)$, dependent on burn-off, B, and total pressure, P, is proposed:

$$M_{BE}(B,P) = f_B(B)\cdot[f_{P,\infty}(P) - f_{P,0}(P)] + f_{P,0}(P)$$

Here $f_B(B)$ is the burn-off dependent factor, $f_{P,\infty}(P)$ is the pressure-dependent factor for high burn-off, $f_{p,0}(P)$ is the pressure-dependent factor for no burn-off.

The following correlations were developed for the pressure-dependent factors $f_{P,0}(P)$ and $f_{P,\infty}(P)$:

$$f_{P,0}(P) = 0.35\cdot\exp(-7.0\times10^{-8}P)$$
$$f_{P,\infty}(P) = 1.70\cdot\exp(-1.8\times10^{-7}P)$$

Here pressure P is in [Pa]. The correlations are shown in Figure 3-4 as solid lines. Since no data was found for total pressure of 55×10^5 Pa, the pressure range for the correlations is limited to $P<55\times10^5$ Pa. For the burn-off dependent factor, the following correlation is used.

$$f_B(B) = \begin{cases} 1-\left(\dfrac{B}{B_\infty}\right)^2 & if\ B < B_\infty \\ 1 & if\ B > B_\infty \end{cases}$$

The correlation is shown in Figure 3-5. The burn-off B is the average depth of the oxidized material [m]. Based on comparison with data of Loenißen, the value of B_∞ is taken as 0.3×10^{-3} m.

The values of $M_{BE}(B,P)$ are tabulated in Table 3-1. The end-point values should be kept outside the tabulated area.

One important fact is that there is a limited amount of experimental data and the data scatter is significant. Therefore, in order to cover all uncertainties one should use a conservative correlation. Based on the considered experimental data, for conservative calculations the Kubaschewski-Heinrich correlation should be used with a constant multiplier of:

$$M_C = 1.8$$

This value of multiplier gives higher oxidation rate than all measurement data considered here.

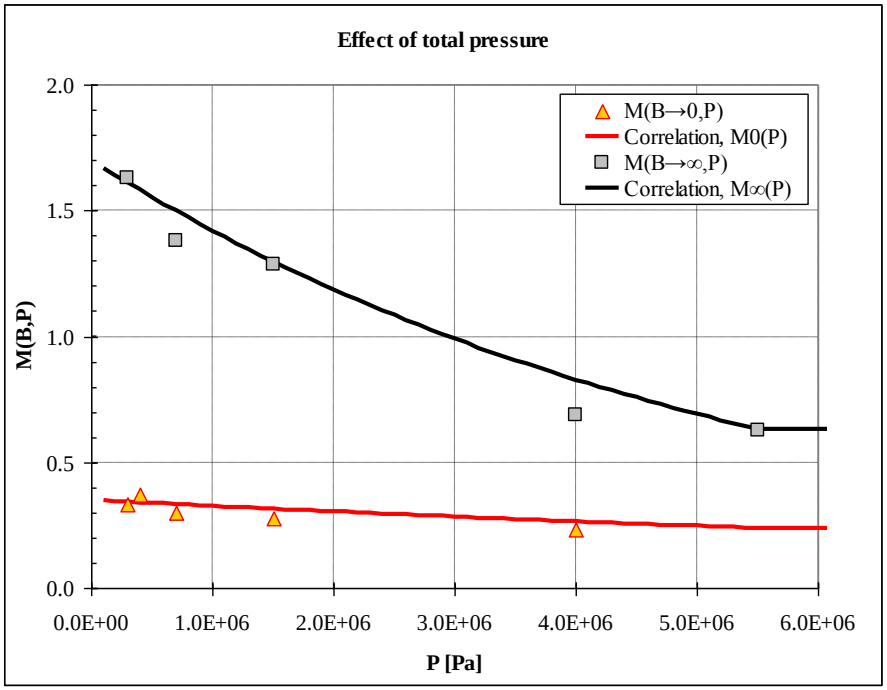

Figure 3-4 : Burn-off and pressure dependent multiplier, $M_{BE}(B,P)$

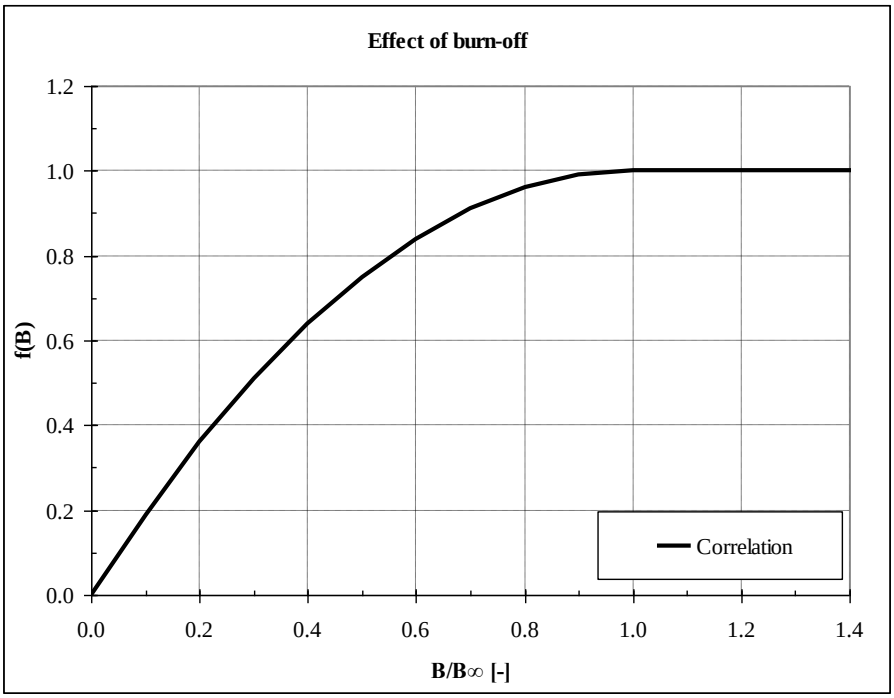

Figure 3-5 : Burn-off factor, $f(B)$

Figure 3-6 shows results of the verification Case 1 (T=1273 K, p = p_{H2O} = 70 bar): Three cases: correlation of Kubaschewski-Heinrich, correlation of Kubaschewski-Heinrich × $M_{BE}(B,P)$ (Best-Estimate), correlation of Kubaschewski-Heinrich × M_C. (Conservative). The times to oxidize the considered layer of graphite (1 mm) are:

- Kubaschewski-Heinrich: τ = 6233 s (see section 3.3.1)
- Kubaschewski-Heinrich × $M_{BE}(B,P)$ (Best-estimate): τ = 10,920 s
- Kubaschewski-Heinrich × M_C (conservative): τ = 3450 s

Table 3-1 : Tabulated values of $M_{BE}(B,P)$

B [m]:		0.00E+00	6.00E-05	1.20E-04	1.80E-04	2.40E-04	3.00E-04
B/B∞ [-]:		0.00	0.20	0.40	0.60	0.80	1.00
f(B/B∞) [-]:		0.00	0.36	0.64	0.84	0.96	1.00
P [Pa]	1.00E+05	0.35	0.82	1.19	1.46	1.62	1.67
	5.00E+05	0.34	0.78	1.12	1.36	1.51	1.55
	1.00E+06	0.33	0.72	1.03	1.24	1.38	1.42
	1.50E+06	0.32	0.67	0.94	1.14	1.26	1.30
	2.00E+06	0.30	0.62	0.87	1.04	1.15	1.19
	2.50E+06	0.29	0.58	0.80	0.96	1.05	1.08
	3.00E+06	0.28	0.54	0.74	0.88	0.96	0.99
	3.50E+06	0.27	0.50	0.68	0.80	0.88	0.91
	4.00E+06	0.26	0.47	0.62	0.74	0.80	0.83
	4.50E+06	0.26	0.44	0.58	0.68	0.74	0.76
	5.00E+06	0.25	0.41	0.53	0.62	0.67	0.69
	5.50E+06	0.24	0.38	0.49	0.57	0.62	0.63

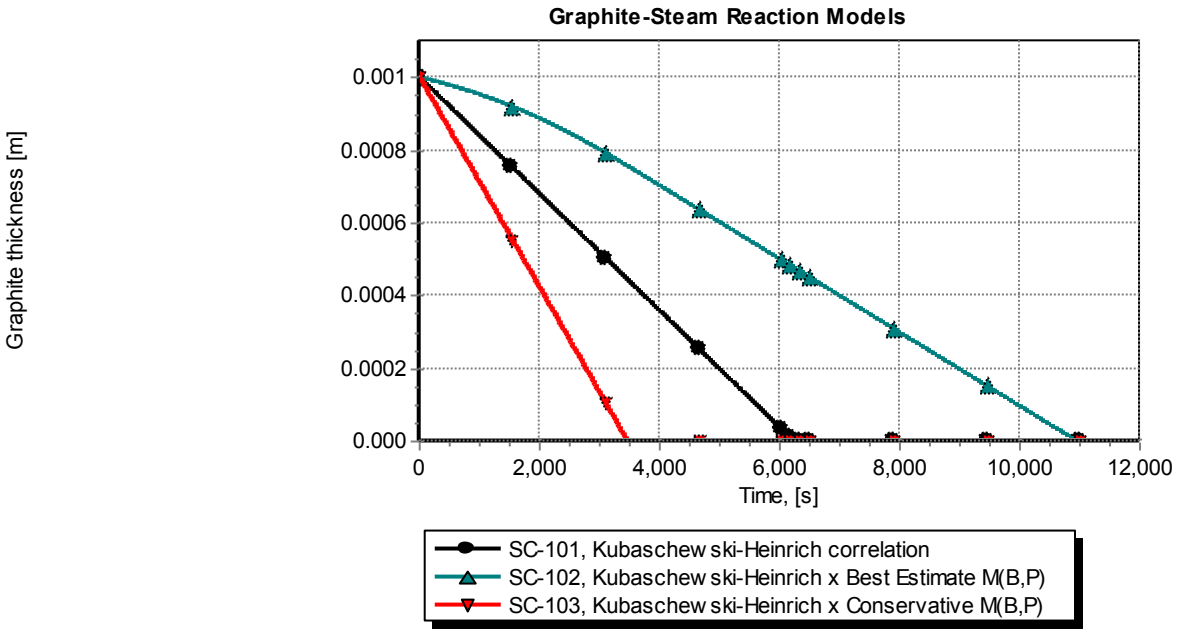

Figure 3-6 : Comparison of correlations - verification test "Case 1"

- Validation of the extended correlation

The results obtained from the correlation of Kubaschewski-Heinrich together with the pressure and burn-off dependent multiplier, $M_{BE}(B,P)$, is compared to the measured data of Loenißen [3] for the 0.474 bar steam pressure cases.

Test Case Loenissen 2 - Influence of M(B,P)

	Burn-off:	1	40	60	80	mg/cm2
	Burn-off:	4.44E-06	1.78E-04	2.67E-04	3.56E-04	m
		1000	1000	1000	1000	˚C
	T=	1273.0	1273.0	1273.0	1273.0	K
	p(H2O)=	0.474	0.474	0.474	0.474	bar
	p(H2)=	0.000	0.000	0.000	0.000	bar
	M(B,P)=	1.00E+00	1.00E+00	1.00E+00	1.00E+00	-
Correlation:	dm/dt=	1.45E+01	1.45E+01	1.45E+01	1.45E+01	mg/cm2-hr
converted to SI:	dm/dt=	4.02E-05	4.02E-05	4.02E-05	4.02E-05	kg/m2-s
directly in SI:	dm/dt=	4.01E-05	4.01E-05	4.01E-05	4.01E-05	kg/m2-s
	ρ=	2250.0	2250.0	2250.0	2250.0	kg/m3

Data from Table 5:

	Burn-off:	~1	~40	~60	~80	mg/cm2
at 3 bar:	dm/dt=	1.33E-03	6.13E-03	6.54E-03	6.45E-03	mg/cm2-s
at 4 bar:	dm/dt=	1.49E-03	-	-	-	mg/cm2-s
at 7 bar:	dm/dt=	1.20E-03	5.14E-03	5.54E-03	-	mg/cm2-s
at 15 bar:	dm/dt=	1.11E-03	-	5.16E-03	4.81E-03	mg/cm2-s
at 40 bar:	dm/dt=	9.44E-04	2.36E-03	2.75E-03	3.12E-03	mg/cm2-s
at 55 bar:	dm/dt=	-	2.14E-03	2.51E-03	-	mg/cm2-s

Converted to SI:

	Burn-off:	~0.0	~2E-4	~3E-4	~4E-4	m
at 3 bar:	dm/dt=	1.33E-05	6.13E-05	6.54E-05	6.45E-05	kg/m2-s
at 4 bar:	dm/dt=	1.49E-05	-	-	-	kg/m2-s
at 7 bar:	dm/dt=	1.20E-05	5.14E-05	5.54E-05	-	kg/m2-s
at 15 bar:	dm/dt=	1.11E-05	-	5.16E-05	4.81E-05	kg/m2-s
at 40 bar:	dm/dt=	9.44E-06	2.36E-05	2.75E-05	3.12E-05	kg/m2-s
at 55 bar:	dm/dt=	-	2.14E-05	2.51E-05	-	kg/m2-s

	M(B,P)			B∞	3.00E-04	
	Burn-off:	0.00E+00	2.00E-04	3.00E-04	4.00E-04	m
P, [Pa]	Burn-off:	0.00E+00	6.67E-01	1.00E+00	1.33E+00	B∞
3.00E+05	M(B,P)=	3.43E-01	1.47E+00	1.61E+00	1.61E+00	-
4.00E+05	M(B,P)=	3.40E-01	1.44E+00	1.58E+00	1.58E+00	-
7.00E+05	M(B,P)=	3.33E-01	1.37E+00	1.50E+00	1.50E+00	-
1.50E+06	M(B,P)=	3.15E-01	1.19E+00	1.30E+00	1.30E+00	-
4.00E+06	M(B,P)=	2.65E-01	7.65E-01	8.27E-01	8.27E-01	-
5.50E+06	M(B,P)=	2.38E-01	5.88E-01	6.32E-01	6.32E-01	-

Correlation * M(B,P)

	Burn-off:	~0.0	~2E-4	~3E-4	~4E-4	m
at 3 bar:	dm/dt=	1.37E-05	5.89E-05	6.46E-05	6.46E-05	kg/m2-s
at 4 bar:	dm/dt=	1.36E-05	-	-	-	kg/m2-s
at 7 bar:	dm/dt=	1.34E-05	5.49E-05	6.01E-05	-	kg/m2-s
at 15 bar:	dm/dt=	1.26E-05	-	5.20E-05	5.20E-05	kg/m2-s
at 40 bar:	dm/dt=	1.06E-05	3.07E-05	3.32E-05	3.32E-05	kg/m2-s
at 55 bar:	dm/dt=	-	2.36E-05	2.53E-05	-	kg/m2-s

Ratio (Correlation/Measurement):

	Burn-off:	~0.0	~2E-4	~3E-4	~4E-4	m
at 3 bar:	corr/exp=	0.97	1.04	1.01	1.00	-
at 4 bar:	corr/exp=	1.09	-	-	-	-
at 7 bar:	corr/exp=	0.90	0.94	0.92	-	-
at 15 bar:	corr/exp=	0.88	-	0.99	0.92	-
at 40 bar:	corr/exp=	0.89	0.77	0.83	0.94	-
at 55 bar:	corr/exp=	-	0.91	0.99	-	-
				Min=	0.77	-23%
Conclusion:				Max=	1.09	9%

Values obtained from the correlation × M(B,P)
need to be multiplied by a factor of 0.77 - 1.09 to match the considered data

It is concluded that:

$$Data = (0.77 \div 1.09) \times Correlation \times M_{BE}(B,P)$$

In other words it represents the data with maximum deviations of –23% and +9%. For comparison, the original correlation had to be multiplied by (0.28 ÷ 1.63), as shown above. That means the maximum deviations were –72% and +63%.

Next, the new correlation is compared to the measured data of Loenißen [3] for the 2.9 bar total pressure cases. The burn-off values are reported on page 95 of reference [3] as 0.7 - 2.5%. Calculations are shown below.

P [Pa]	Correlatio	Correlation, M∞(P)
2.90E+05	*0.34*	*1.61*

B [%]	B [mm]	B/B∞ [-]	Correlation	M(B,P)
0.7	1.40E-01	0.47	0.72	1.25
1.3	2.60E-01	0.87	0.98	1.59
1.9	3.80E-01	1.00	1.00	1.61
2.5	5.00E-01	1.00	1.00	1.61

based on Lohnert: 0.8% corresponds to 0.16 mm

0.8	0.16

Test Case Loenissen 1

		1000	1000	1000	1000	˚C	
	T=	1273.0	1273.0	1273.0	1273.0	K	
	p(H2O)=	0.066	0.243	0.394	0.973	bar	
	p(H2)=	0.000	0.000	0.000	0.000	bar	
	M(B,P)=	1.25E+00	1.59E+00	1.61E+00	1.61E+00	-	P=2.9 bar
Correlation:	dm/dt=	7.60E+00	1.71E+01	2.15E+01	3.20E+01	mg/cm2-hr	
converted to SI:	dm/dt=	2.11E-05	4.76E-05	5.97E-05	8.89E-05	kg/m2-s	
directly in SI:	dm/dt=	2.11E-05	4.77E-05	5.98E-05	8.90E-05	kg/m2-s	
Data, p. 95:	dm/dt=	1.78E-03	4.17E-03	4.39E-03	9.72E-03	mg/cm2-s	
	dm/dt=	1.78E-05	4.17E-05	4.39E-05	9.72E-05	kg/m2-s	
Ratio:		0.84	0.87	0.73	1.09		

Conclusion:
Values obtained from the investigated correlation
need to be multiplied by a factor of 0.73 - 1.09 to match the considered data

It is concluded that:

$$Data = (0.73 \div 1.09) \times Correlation$$

In other words it represents the data with maximum deviations of –27% and +9%. For comparison, the original correlation had to be multiplied by (1.05 ÷ 1.76), as shown above. That means the maximum deviations were +5% and +76%.

Next, the new correlation is compared to the measured data of Abel Holden earlier in this section, next to the original correlation in the column marked “best est.”. The value at high burn-off and 1 bar pressure (1.67 - see Table 3-1) is taken. The multiplier is 1.00, compared to 1.66 in the original correlation. That means the error is reduced from 66% to 0%.

Finally, the new correlation is compared to the measured data of Xinli Yu, Suyuan Yu earlier in this section, next to the original correlation in the column marked “best est.”. The value at high burn-off and high pressure (0.63 - see Table 3-1) is taken. The multiplier is 1.15, compared to 0.73 in the original correlation. That means the error is reduced from 27% to 15%.

It is shown that the new correlation gives better agreement with all considered experimental data. Therefore this correlation is recommended for best estimate calculations.

- Summary of graphite-steam reaction validation

Comparison of the results obtained using the Kubaschewski-Heinrich correlation against available measurement data, showed that:

$$Data = (0.28 \div 1.76) \times Correlation$$

The correlation does not include the burn-off factor and total pressure. Based on the performed comparisons, a multiplier dependent on burn-off and total pressure, $M_{BE}(B,P)$, is proposed. When the correlation of Kubaschewski-Heinrich is applied together with $M_{BE}(B,P)$, the calculated results are in agreement with available data with maximum deviations of –27% and +15%.

$$Data = (0.73 \div 1.15) \times Correlation \times M_{BE}(B,P)$$

The improvement of accuracy, as well as experimental conditions for each case are shown in Table 3-2. Based on the experimental conditions, the range of application of the new correlation is:

- temperatures: T 1000 K ÷1300 K (750˚C ÷ 1100˚C)
- pressures: p 10^5 Pa ÷ 55×10^5 Pa (1 ÷ 55 bar)
- steam pressures p_{H2O} 14 ÷ 10^5 Pa (0.00014 ÷ 1.0 bar)

Table 3-2 : Graphite-steam oxidation - experimental condition and correlation accuracy

Test	Temperature	Pressure	Steam pressure	Maximum deviation	
				Original corr. $M(B,P)$=1.0	New corr. $M(B,P)$=B.E.
Leonißen 1 Leonißen 2 Abel-Holden	1273 K (1000˚C) 1273 K (1000˚C) 1311 K (1038˚C)	2.9 bar 3 ÷ 55 bar 1.0 bar	0.066 ÷ 0.0973 bar 0.474 bar 1.0 bar	+5% ÷ +76% –72% ÷ +23% +66%	–27% ÷ +9% –23% ÷ +9% 0%
Yu (code-to-code)	1023 K (750˚C)	0.00014	-	+27%	+15%

The recommendations are:

- For best estimate results the Kubaschewski-Heinrich correlation should be used with the Best-Estimate multiplier, $M_{BE}(B,P)$, proposed here.
- For conservative results the Kubaschewski-Heinrich correlation should be used with a constant multiplier of M_C=1.8, which gives higher oxidation rate than all measurement data considered here.

4 Secondary Reactions

4.1 Secondary Heterogeneous Reaction

The secondary heterogeneous reaction:

$$C + CO_2 \rightarrow 2CO$$

Reference [8] recommends the correlation from Moormann [9], to calculate the reaction kinetics. The correlation is:

$$\frac{dm}{dt} = \frac{14.5 \cdot \exp(-25{,}000/T) \cdot p_{CO2}}{1 + 3.4 \times 10^{-5} \cdot \exp(7000/T) \cdot (p_{CO2})^{0.5}}$$

Here temperature is in [K], pressure is in [Pa], and reaction rate in [mg/cm^2-s]. The reaction rate determines the mass of graphite (carbon) consumed. The formula is converted to SI units:

$$\frac{dm}{dt} = \frac{0.145 \cdot \exp(-25{,}000/T) \cdot p_{CO2}}{1 + 3.4 \times 10^{-5} \cdot \exp(7000/T) \cdot (p_{CO2})^{0.5}}$$

The reaction heat, –172.5 kJ/mol = –172.5×10^6 [J/kmol] = –14.4×10^6 [J/kg] (per unit mass of oxidized C).

For the purpose of test calculations in SPECTRA, the reaction rate is defined using the temperature-dependent factor $K_T(T)$, the correction to the temperature-dependent factor $C_T(T,p_i)$, and the pressure-dependent factor, $K_p(p_1)$:

- Temperature-dependent coefficient, $K_T(T)$:

$$K_T = 0.145 \cdot \exp\left[-\frac{25{,}000}{T}\right]$$

- Correction to temperature-dependent coefficient, $C_T(T, p_i)$:

$$C_T = \frac{1}{1 + 3.4 \cdot 10^{-5} \cdot \exp\left[\frac{7000}{T}\right] \cdot (p_{CO2})^{0.5}}$$

- Pressure-dependent coefficient, $K_p(p_1)$:

$$K_p = (p_{CO2})^{1.0}$$

It is questionable if this correlation holds in the higher pressure range (and variety of gas mixtures), since it was determined for 10^5 Pa pressure and is more relevant in the case of air ingress. It is recommended to do a sensitivity study by performing water ingress scenarios with and without this model, to estimate the effect of this reaction on overall system behavior.

SPECTRA V&V on this reaction was not performed within the present project and is not discussed here, because this was done in the past, using available data from the air ingress tests.

4.2 Secondary Homogeneous Reaction

The secondary homogeneous reaction is:

$$CO + H_2O \rightarrow CO_2 + H_2$$

Reference [8] recommends the correlation of Graven and Long [10], to calculate the reaction kinetics. The correlation is:

$$\dot{n}_{CO2} = \frac{2.32 \cdot 10^{14} \cdot \exp\left(-\frac{33{,}000}{T}\right) \cdot c_{H2O} \cdot \sqrt{c_{CO}}}{\sqrt{1 + 1.2 \cdot 10^{4} \cdot c_{H2}}}$$

The reaction rate here is in [mol/m^3-s]. The equation is converted to give the rate per unit mass of consumed CO:

$$\frac{dm}{dt} = \frac{1.04 \cdot 10^{8} \cdot \exp\left(-\frac{33{,}000}{T}\right) \cdot c_{H2O} \cdot \sqrt{c_{CO}}}{\sqrt{1 + 1.2 \cdot 10^{4} \cdot c_{H2}}}$$

All above parameters are in SI units, temperature in [K], reaction rate in [kg/m^2-s]. The reaction rate determines the mass of CO gas consumed. The reaction heat, –41.2 kJ/mol = –41.2×10^6 [J/kmol] = –1.47×10^6 [J/kg] (per unit mass of reacted CO).

This reaction cannot be modeled in SPECTRA using the Material Oxidation Package (=OX=), because within OX only surface reactions are considered. This is a gas reaction occurring in the bulk gas volume. In the current SPECTRA version the gas reactions are not considered. However, such reaction can be taken into account using Control Volume mass and energy sources. Such sources may be defined using Tabular or Control Functions. Negative mass sources are possible. Therefore the user can easily define the homogenous reaction using a set of Control Functions.

Currently no V&V was performed for this secondary reaction. The relative importance of this reaction compared to other reactions will be a subject of sensitivity analysis.

5 Summary and Conclusions

5.1 Summary

The recommended correlation for the reaction kinetics of the primary heterogeneous reaction,

$$C + H_2O \rightarrow H_2 + CO$$

is as follows:

$$\frac{dm}{dt} = K(T, p_i) \cdot M(B,P)$$

The main part is the correlation of Kubaschewski-Heinrich converted to SI units:

$$K(T, p_i) = \frac{1.12 \cdot 10^4 \cdot \exp\left[-\frac{30788}{T}\right] \cdot (p_{H2O})^{0.44}}{1 + 2.37 \cdot 10^{-7} \cdot \exp\left[\frac{14552}{T}\right] \cdot (p_{H2})^{0.9} (p_{H2O})^{-0.4}}$$

- Best Estimate

  For best estimate calculations, a multiplier depending on burn-off and total pressure is defined as:

$$M_{BE}(B,P) = f_B(B) \cdot [f_{P,\infty}(P) - f_{P,0}(P)] + f_{P,0}(P)$$

  Pressure-dependent factors:

$$f_{P,0}(P) = 0.35 \cdot \exp(-7.0 \times 10^{-8} P)$$
$$f_{P,\infty}(P) = 1.70 \cdot \exp(-1.8 \times 10^{-7} P)$$

  The correlations for pressure-dependent factor are applicable for P<55×10^5 Pa. The burn-off dependent factor is defined as:

$$f_B(B) = \begin{cases} 1 - \left(\frac{B}{B_\infty}\right)^2 & if \ B < B_\infty \\ 1 & if \ B > B_\infty \end{cases}$$

  The burn-off B is the average depth of the oxidized material [m]. The value of B_∞ is 0.3×10^{-3} m.

  .Alternatively the multiplier $M_{BE}(B,P)$ can be taken from Table 3-1.

  The maximum deviation of the correlation results and experimental data is –27% and +15%. The range of application of the correlation is:

  - temperatures: T 1000 K ÷1300 K
  - pressures: p 10^5 Pa ÷ 55×10^5 Pa
  - steam pressures p_{H2O} 14 ÷ 10^5 Pa

- Conservative

  For conservative calculations, a constant multiplier is recommended:

$$M_C = 1.8$$

All above parameters are in SI units, temperature in [K], pressure in [Pa], reaction rate in [kg/m^2-s]. The reaction rate determines the mass of graphite (carbon) consumed.

The reaction heat, 131.3 kJ/mol = 131.3×10^6 [J/kmol] = 10.9×10^6 [J/kg] (per unit mass of oxidized C).

5.2 Conclusions

Within the ARCHER project, WP22, an analysis of consequences of the water ingress into the HTR reactor will be analyzed in the future with the system code SPECTRA. The present report describes a preparatory work, including:

- Review of reactions that may take place during water ingress
- Selection of models applicable for these reactions
- Making necessary extensions to the Material Oxidation Package in SPECTRA, to make sure that it will be possible to model all these reactions.
- Comparison of models with available data. The correlation of Kubaschewski-Heinrich was compared to the available measured data. The correlation takes into account the effect of temperature, steam partial pressure and hydrogen partial pressure. The correlation does not take into account the effect of burn-off and total pressure. Within the current work an extension of the Kubaschewski-Heinrich correlation is proposed that takes into account these effects. This extension has a form of a multiplier on the original correlation. The value of this multiplier depends of the burn-off and total pressure:

  $$M_{BE}(B,P)$$

  Comparison of the correlation of Kubaschewski-Heinrich applied together with $M_{BE}(B,P)$ allows to reduce significantly the discrepancies between the correlation and the measured data. This correlation will be used for best estimate calculations. For conservative calculations the multiplier of

  $$M_C = 1.8$$

  will be used.

As a next step, the SPECTRA model of the HTR reference plant will be built and a water ingress scenario will be analyzed.

6 References

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7 Annexes

Annex 1 – Document approval by beneficiaries' internal QA

7.1 Annex 1: Document approval by beneficiaries' internal QA

Fill involved beneficiaries as appropriate (mandatory for Milestones and Deliverables, but optional for other document type)

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